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(54) Title: A PROCESS FOR PREPARING A SILVER CATALYST, THE CATALYST, AND ITS USE FOR OLEFFIN OXIDATION

(57) Abstract: A process for preparing a catalyst comprising silver, a rhenium component, and a rhenium co-promoter on a support, which process comprises - depositing the rhenium co-promoter on the support prior to or simultaneously with depositing silver on the support, and - depositing the rhenium component on the support after depositing silver on the support; the catalyst; and a process for preparing an olefin oxide by reacting an olefin with oxygen in the presence of the catalyst. They preferred rhenium co-promoter is tungsten.



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A PROCESS FOR PREPARING A SILVER CATALYST, THE CATALYST, AND ITS USE FOR
OLEFIN OXIDATION

FIELD OF THE INVENTION

5 The invention relates to a process for preparing a high-selectivity olefin epoxidation catalyst, the catalyst per se and a process for the epoxidation of an olefin in which the catalyst is used.

BACKGROUND OF THE INVENTION

10 In olefin epoxidation an olefin is reacted with oxygen to form an olefin epoxide, using a silver-based catalyst. The olefin oxide may be reacted with water, an alcohol or an amine to form a 1,2-diol, a 1,2-diol ether or an alkanolamine. Thus, 1,2-diols, 1,2-diol ethers and
15 alkanolamines may be produced in a multi-step process comprising olefin epoxidation and converting the formed olefin oxide with water, an alcohol or an amine.

 Conventional silver-based catalysts have provided the olefin oxide notoriously in a low selectivity. Also, the
20 catalysts are subject to an aging-related performance decline during normal operation. The aging manifests itself by a reduction in the activity of the catalyst. Usually, when a reduction in activity of the catalyst is manifest, the reaction temperature is increased in order to compensate for
25 the reduction in activity. The reaction temperature may be increased until it becomes undesirably high, at which point in time the catalyst is deemed to be at the end of its lifetime and would need to be exchanged.

 Over the years much efforts have been devoted to
30 improving epoxidation catalysts in their performance, for example in respect of their initial activity and selectivity, and in respect of their stability performance, that is their resistance against the aging-related performance decline. In

some instances, solutions have been found in improved compositions of the catalysts.

For example, modern silver-based catalysts are highly selective towards olefin oxide production. Such so-called high-selectivity catalysts may comprise as their active components silver, and one or more high-selectivity promoters, for example components comprising rhenium, and rhenium co-promoters, as disclosed in US-A-4761394 and US-A-4766105.

In particular the high-selectivity catalysts are subject to an aging-related performance decline during normal operation and they tend to be exchanged more frequently than the conventional catalysts. It goes without saying that from an economical point of view it is highly desirable to extend the lifetime of high-selectivity catalysts as much as possible.

SUMMARY OF THE INVENTION

The present invention provides a process for preparing a catalyst comprising silver, a rhenium component, and a rhenium co-promoter on a support, which process comprises

- depositing the rhenium co-promoter on the support prior to or simultaneously with depositing silver on the support, and
- depositing the rhenium component on the support after depositing silver on the support.

The present invention also provides a catalyst comprising silver, a rhenium component, and a rhenium co-promoter deposited on a support which catalyst is obtainable by the process for preparing a catalyst according to the invention.

The present invention also provides a process for preparing an olefin oxide by reacting an olefin with oxygen in the presence of a catalyst which is obtainable by the process for preparing a catalyst according to the invention.

The present invention also provides a method of using an olefin oxide for making a 1,2-alkanediol, a 1,2-alkanediol ether or a 1,2-alkanolamine comprising converting the olefin oxide into the 1,2-alkanediol, the 1,2-alkanediol ether, or the 1,2-alkanolamine, wherein the olefin oxide has been obtained by the process for preparing an olefin oxide according to this invention.

DETAILED DESCRIPTION OF THE INVENTION

When a catalyst is prepared in accordance with this invention an advantage is achieved in the performance of the catalyst, when compared with the performance obtained when the catalyst is prepared by depositing the rhenium co-promoter and the rhenium component simultaneously on the support. The advantage may be found, for example, in an improved activity of the catalyst and an improved resistance against performance decline, in particular activity and selectivity.

US-A-4766105 discussed the possibility that rhenium may be deposited at the same time that silver is added, or before or later; or at the same time that the rhenium co-promoter is added, or before or later. US-A-4766105 mentioned that, amongst other examples, there may be found alkali and rhenium co-promoter on the support and rhenium on the catalyst. It is appreciated that rhenium may be found on the catalyst as a result of depositing rhenium on the support at the same time that silver is added, or before or later. There is nothing in US-A-4766105 suggesting or teaching that the order of depositing silver, rhenium and rhenium co-promoter on the support could possibly influence the catalyst performance.

The support for use in this invention may be based on a wide range of materials. Such materials may be natural or artificial inorganic materials and they may include refractory materials, silicon carbide, clays, zeolites,

charcoal and alkaline earth metal carbonates, for example calcium carbonate. Preferred are refractory materials, such as alumina, magnesia, zirconia and silica. The most preferred material is α -alumina. Typically, the support
5 comprises at least 85 %w, more typically 90 %w, in particular 95 %w α -alumina, frequently up to 99.9 %w α -alumina, relative to the weight of the support. Other components of the α -alumina support may comprise, for example, silica, alkali metal components, for example sodium and/or potassium
10 components, and/or alkaline earth metal components, for example calcium and/or magnesium components.

The surface area of the support may suitably be at least 0.1 m²/g, preferably at least 0.3 m²/g, more preferably at least 0.5 m²/g, and in particular at least 0.6 m²/g, relative
15 to the weight of the support; and the surface area may suitably be at most 10 m²/g, preferably at most 5 m²/g, and in particular at most 3 m²/g, relative to the weight of the support. "Surface area" as used herein is understood to relate to the surface area as determined by the B.E.T.

(Brunauer, Emmett and Teller) method as described in the
20 Journal of the American Chemical Society 60 (1938) pp. 309-316. High surface area supports, in particular when they are α -alumina supports optionally comprising in addition silica, alkali metal and/or alkaline earth metal components, provide
25 improved performance and stability of operation.

The water absorption of the support is typically in the range of from 0.2 to 0.8 g/g, preferably in the range of from 0.3 to 0.7 g/g. A higher water absorption may be favored in
30 view of a more efficient deposition of silver and further elements, if any, on the support by impregnation. However, at a higher water absorption, the support, or the catalyst made therefrom, may have lower crush strength. As used herein, water absorption is deemed to have been measured in

accordance with ASTM C20, and water absorption is expressed as the weight of the water that can be absorbed into the pores of the support, relative to the weight of the support.

The support is typically a calcined, i.e. sintered, support, preferably in the form of formed bodies, the size of which is in general determined by the dimensions of a reactor in which they are to be deposited. Generally however it is found very convenient to use particles such as formed bodies in the form of powdery particles, trapezoidal bodies, cylinders, saddles, spheres, doughnuts, and the like. The cylinders may be solid or hollow, straight or bent, and they may have their length and cross-sectional dimensions about the same and from 5 to 15 mm.

The performance of the catalyst may be enhanced if the support is washed before depositing catalyst ingredients on the support. On the other hand, unwashed supports may also be used successfully. A useful method for washing the support comprises washing the support in a continuous fashion with hot, demineralised water, until the electrical conductivity of the effluent water does not further decrease. A suitable temperature of the demineralised water is in the range of 80 to 100 °C, for example 90 °C or 95 °C. Alternatively, the support may be washed with base and subsequently with water. Reference may be made to US-B-6368998, which is incorporated herein by reference.

The washing is intended to remove soluble residues from the support, in particular soluble residues which can be measured as nitric acid extractable components of the support. A method of measuring the content of nitric acid extractable components involves extracting a 10-gram sample of the support by boiling it with a 100 ml portion of 10 %w nitric acid for 30 minutes (1 atm., i.e. 101.3 kPa) and determining in the combined extracts the relevant components

by using a known method, for example atomic absorption spectroscopy. Reference is made to US-A-5801259, which is incorporated herein by reference. The support for use in this invention, or more generally a support for preparing

5 silver-based catalysts for use in the preparation of an olefin oxide from the olefin and oxygen, has typically a content of nitric acid extractable components (as the weight of the metal, or SiO_2), relative to the weight of the support; in parts per million (ppmw) as follows:

0 sodium: less than 500 ppmw, preferably less than 400 ppmw, and/or

potassium: less than 150 ppmw, preferably less than 100 ppmw, and/or

5 calcium: less than 400 ppmw, preferably less than 300 ppmw, and/or

aluminum: less than 1100 ppmw, preferably less than 800 ppmw, and/or

silicate: less than 1000 ppmw, preferably less than 800 ppmw.

10 If the support is a calcined support, in particular an α -alumina support, re-calcining the support may be an alternative method of reducing the content of nitric acid extractable components of the support. Suitably, the calcination is carried out by heating a precursor of the

15 support at a temperature in the range of from 1000 to 1600 °C, preferably 1200 to 1500 °C, typically for a period of from 1 to 50 hours, and more typically from 10 to 40 hours. Suitably, the re-calcination may be carried out by heating the support at a similar temperature and for a

20 similar period of time as in the calcination. Preferably, the conditions of re-calcination are somewhat less severe than the conditions of calcination, for example in that the temperature is 50 °C or 100 °C lower and/or the time is

shorter. The atmosphere applied in the calcination or re-calcination is not critical. For example, an inert atmosphere may be applied, such as nitrogen or argon, or an oxygen containing atmosphere may be applied such as air or a mixture of air and nitrogen.

In a preferred embodiment, amongst others, a base (hereinafter "first base") may be deposited on the support before depositing catalyst ingredients on the support. Suitably, the first base has a pK_b of at most 3.5, when measured in water at 25 °C, preferably, the pK_b is at most 2, more preferably at most 1. A suitable first base may be a hydroxide, for example lithium hydroxide or a quaternary ammonium hydroxide, typically tetramethylammonium hydroxide or tetraethylammonium hydroxide, or an alkoxide, typically lithium methoxide or aluminum trimethoxide. The quantity of the first base may be up to 1000 mmole/kg support, for example in the range of from 0.5 to 500 mmole/kg support, preferably in the range of from 1 to 100 mmole/kg, more preferably in the range of from 5 to 50 mmole/kg, for example 10, 14, 20 or 30 mmole/kg.

The skilled person will appreciate that a base may be multibasic, that is having a multitude of basic functionalities. For example, a base may be dibasic or tribasic. The base properties of a multibasic compound may be specified using more than one pK_b value. It is to be understood that, as used herein, in the case of a multibasic compound the number of moles of base having a pK_b as specified includes the total number of moles of basic functionalities having the specified pK_b value.

The first base may be deposited on the support by impregnating the support with a solution containing a sufficient amount of the first base. After impregnation, the support may be dried, typically at a temperature of at most

300 °C, preferably at most 250 °C, more preferably at most 200 °C, and suitably at a temperature of at least 20 °C, preferably at least 50 °C, more preferably at least 80 °C, suitably for a period of time of at least 1 minute,

5 preferably at least 2 minutes, and suitably for a period of time of at most 60 minutes, preferably at most 30 minutes, more preferably at most 15 minutes. The application of more severe conditions, up to the calcination conditions, as described hereinbefore, may be considered in addition to, or
10 in place of, the conditions described for the drying.

The volume of impregnation solutions described herein may be such that the support is impregnated until a point of incipient wetness of the support has been reached.

Alternatively, a larger volume may be used and the surplus of
15 solution may be removed from the wet support, for example by decantation or centrifugation. Amongst others, the impregnation solutions may comprise an alcoholic diluent, for example methanol or ethanol, or it may be aqueous. This includes that mixed diluents may be used.

20 The preparation of silver-based catalysts is known in the art and the known methods are applicable to the preparation of the catalyst in accordance with the invention. Methods of depositing silver on the support include impregnating the support with a silver compound containing
25 cationic silver and performing a reduction to form metallic silver particles. Reference may be made, for example, to US-A-5380697, US-A-5739075, EP-A-266015, and US-B-6368998, which US patents are incorporated herein by reference. Typically, in the normal practice of this invention, the rhenium co-
30 promoter is deposited on the support prior to or simultaneously with the deposition of silver metal on the support, and rhenium component is deposited on the support

after deposition of at least a portion of silver metal on the support.

The reduction of cationic silver to metallic silver may be accomplished during a step in which the catalyst is dried, so that the reduction as such does not require a separate process step. This may be the case if the silver containing impregnation solution comprises a reducing agent, for example, an oxalate, as described in the Examples hereinafter. Such drying step is suitably carried out at a reaction temperature of at most 300 °C, preferably at most 280 °C, more preferably at most 260 °C, and suitable at a reaction temperature of at least 200 °C, preferably at least 210 °C, more preferably at least 220 °C, suitably for a period of time of at least 1 minute, preferably at least 2 minutes, and suitably for a period of time of at most 20 minutes, preferably at most 15 minutes, more preferably at most 10 minutes.

In preferred embodiment, amongst others, the silver containing impregnation solution comprises an added base (hereinafter "second base"), typically a base having a pK_b of at most 3.5, when measured at 25 °C, preferably at most 2, more preferably at most 1. A suitable second base may be a hydroxide, for example lithium hydroxide or a quaternary ammonium hydroxide, typically tetramethylammonium hydroxide or tetraethylammonium hydroxide, or an alkoxide, typically lithium methoxide or aluminum trimethoxide. Preferably, the pH of the impregnation solution is at least 13.2, more preferably at least 14, in particular at least 14.5. As used herein, "pH" is the pH as measured at 20 °C. The measured pH may be different from the true pH, because the medium of the solution of which the pH is measured may not be aqueous. The second base may be added to the impregnation solution in a quantity in the range of from 1 to 1000 mmole/kg support,

preferably in the range of from 5 to 500 mmole/kg, more preferably in the range of from 10 to 100 mmole/kg, for example 50 or 75 mmole/kg.

The second base may or may not be the same as the first base. The second base may be deposited on the support independent of whether or not the first base is deposited on the support. The first base may be deposited on the support independent of whether or not the second base is deposited on the support.

Appreciable catalytic activity is obtained by employing a silver content of the catalyst of at least 10 g/kg, relative to the weight of the catalyst. Preferably, the catalyst comprises silver in a quantity of from 50 to 500 g/kg, more preferably from 100 to 400 g/kg, for example 105 g/kg, or 120 g/kg, or 190 g/kg, or 250 g/kg, or 350 g/kg, relative to the weight of the catalyst. The silver compound may be employed in the impregnation solution in a quantity sufficient to provide in a single deposition of silver a catalyst having a content of silver as disclosed herein. In that case, the rhenium co-promoter may be deposited prior to or simultaneously with the single deposition of silver and the rhenium component may be deposited after depositing silver.

In particular in the preparation of a catalyst having a relatively high silver content, for example in the range of from 150 to 500 g/kg, in particular from 200 to 400 g/kg, on total catalyst, it may be advantageous to apply multiple depositions of silver. Silver may be deposited in three or more portions, and preferably in two portions. For example, a portion of silver may be deposited together with the deposition of the rhenium co-promoter, and another portion may be deposited together with the deposition of the rhenium component. In an alternative, a portion of silver may be

deposited together with the deposition of the rhenium co-promoter, a second portion may be deposited, and thereafter a third portion of silver may be deposited together with the rhenium component. In yet another alternative, a portion of
5 silver may be deposited together with the deposition of the rhenium co-promoter, a second portion may be deposited together with the deposition of the rhenium component, and a third portion may be deposited together with the deposition of further rhenium component. Without wishing to be bound by
10 theory, it is believed that in embodiments in which dopants (for example the rhenium component and/or the rhenium co-promoter) are deposited simultaneously with the deposition of a portion of silver, as opposed to deposition separate from the deposition of silver, a more favourable distribution of
15 the dopant over the support will be achieved. Such embodiments are therefore preferred, as they will yield better catalysts. Silver may be divided over the various depositions, such that in each deposition a silver solution of the same silver concentration is employed. It is
20 preferred, however, to employ in a later deposition a silver solution having a higher silver concentration than in a previous deposition.

The rhenium component may typically be present in a quantity of at least 0.01 mmole/kg, more typically at least
25 0.1 mmole/kg, and preferably at least 0.5 mmole/kg, calculated as the quantity of rhenium relative to the weight of the catalyst. The rhenium component may be present in a quantity of at most 50 mmole/kg, preferably at most
10 mmole/kg, more preferably at most 5 mmole/kg, calculated
30 as the quantity of rhenium relative to the weight of the catalyst. The form in which the rhenium component may be deposited onto the support is not material to the invention. For example, the rhenium component may suitably be provided

as an oxide or as an oxyanion, for example, as a rhenate or perrhenate, in salt or acid form. The rhenium component may be employed in the invention in a quantity sufficient to provide a catalyst having a rhenium content as disclosed
5 herein.

The rhenium co-promoter may suitably be selected from components comprising one or more of tungsten, chromium, molybdenum, sulfur, phosphorus, boron, and mixtures thereof. Preferably, the rhenium co-promoter is selected from
10 components comprising one or more of tungsten, chromium, molybdenum, sulfur, and mixtures thereof. It is particularly preferred that the rhenium co-promoter comprises a tungsten component.

The rhenium co-promoter may typically be present in a
15 total quantity of at least 0.01 mmole/kg, more typically at least 0.1 mmole/kg, and preferably at least 0.5 mmole/kg, calculated as the element (i.e. the total of tungsten, chromium, molybdenum, sulfur, phosphorus and/or boron), relative to the weight of the catalyst. The rhenium co-
20 promoter may be present in a total quantity of at most 50 mmole/kg, preferably at most 10 mmole/kg, more preferably at most 5 mmole/kg, on the same basis. In the practice of this invention at least a portion of the rhenium co-promoter is deposited on the support prior to depositing the rhenium
25 component. The form in which the rhenium co-promoter may be deposited on the support is not material to the invention. For example, it may suitably be provided as an oxide or as an oxyanion, for example, as a sulfate, borate or molybdate, in salt or acid form. The rhenium co-promoter may be employed
30 in the invention in a quantity sufficient to provide a catalyst having a content of the rhenium co-promoter as disclosed herein.

The catalyst preferably comprises silver, a rhenium component, a rhenium co-promoter, and a component comprising a further element. Eligible further elements may be selected from the group of nitrogen, fluorine, alkali metals, alkaline earth metals, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium and germanium and mixtures thereof. Preferably the alkali metals are selected from lithium, potassium, rubidium and cesium. Most preferably the alkali metal is lithium, potassium and/or cesium. Preferably the alkaline earth metals are selected from calcium and barium. Typically, the further element is present in the catalyst in a total quantity of from 0.01 to 500 mmole/kg, more typically from 0.05 to 100 mmole/kg, calculated as the element on the weight of the catalyst.

Where possible, the component comprising the further element may suitably be provided as an oxide or as an oxyanion, for example, as a sulfate, nitrate, nitrite, borate or molybdate, in salt or acid form. Salts of alkali metals or alkaline earth metals are suitable. The component comprising the further element may be employed in the invention in a quantity sufficient to provide a catalyst having a content of the further element as disclosed herein. The component comprising the further element may be deposited on the support prior to, together with or after the deposition of silver; prior to, together with or after the deposition of the rhenium component; and/or prior to, together with or after the deposition of the rhenium co-promoter.

The content of alkali metal components of the catalyst generally influences the performance of the catalyst in the preparation of an olefin oxide from the olefin and oxygen. In one aspect, the performance may relate to the ability to operate the catalyst outside the conditions of a runaway reaction, that is total oxygen conversion and locally a very

high catalyst temperature. In certain embodiments relating to catalysts which have a content of a rhenium component of less than 1.5 mmole/kg, in particular less than 1 mmole/kg, calculated as the quantity of rhenium relative to the weight of the catalyst, a cesium component may be applied in a quantity higher than the quantity that may be needed for optimal catalyst performance in terms of activity and selectivity (for example, 700 ppmw, instead of 500 ppmw, as the weight of cesium relative to the weight of the catalyst) with the effect that conditions of a runaway reaction are more easily avoided.

As used herein, the quantity of alkali metal present in the catalyst is deemed to be the quantity in so far as it can be extracted from the catalyst with de-ionized water at 100 °C. The extraction method involves extracting a 10-gram sample of the catalyst three times by heating it in 20 ml portions of de-ionized water for 5 minutes at 100 °C and determining in the combined extracts the relevant metals by using a known method, for example atomic absorption spectroscopy.

As used herein, the quantity of alkaline earth metal present in the catalyst is deemed to be the quantity in so far as it can be extracted from the catalyst with 10 %w nitric acid in de-ionized water at 100 °C. The extraction method involves extracting a 10-gram sample of the catalyst by boiling it with a 100 ml portion of 10 %w nitric acid for 30 minutes (1 atm., i.e. 101.3 kPa) and determining in the combined extracts the relevant metals by using a known method, for example atomic absorption spectroscopy.

Reference is made to US-A-580 1259, which is incorporated herein by reference.

Although the present epoxidation process may be carried out in many ways, it is preferred to carry it out as a gas

phase process, i.e. a process in which the feed is contacted in the gas phase with the catalyst which is present as a solid material, typically in a packed bed. Generally the process is carried out as a continuous process.

5 The olefin for use in the present epoxidation process may be any olefin, such as an aromatic olefin, for example styrene, or a di-olefin, whether conjugated or not, for example 1,9-decadiene or 1,3-butadiene. Typically, the olefin is a monoolefin, for example 2-butene or isobutene.

10 Preferably, the olefin is a mono- α -olefin, for example 1-butene or propylene. The most preferred olefin is ethylene.

 The olefin concentration in the feed may be selected within a wide range. Typically, the olefin concentration in the feed will be at most 80 mole-%, relative to the total
15 feed. Preferably, it will be in the range of from 0.5 to 70 mole-%; in particular from 1 to 60 mole-%, on the same basis. As used herein, the feed is considered to be the composition which is contacted with the catalyst.

 The present epoxidation process may be air-based or
20 oxygen-based, see "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd edition, Volume 9, 1980, pp. 445-447. In the air-based process air or air enriched with oxygen is employed as the source of the oxidizing agent while in the oxygen-based processes high-purity (at least 95 mole-%)
25 oxygen is employed as the source of the oxidizing agent. Presently most epoxidation plants are oxygen-based and this is a preferred embodiment of the present invention.

 The oxygen concentration in the feed may be selected within a wide range. However, in practice, oxygen is
30 generally applied at a concentration which avoids the flammable regime. Typically, the concentration of oxygen applied will be within the range of from 1 to 15 mole-%, more typically from 2 to 12 mole-% of the total feed.

In order to remain outside the flammable regime, the concentration of oxygen in the feed may be lowered as the concentration of the olefin is increased. The actual safe operating ranges depend, along with the feed composition, also on the reaction conditions such as the reaction temperature and the pressure.

An organic halide may be present in the feed as a reaction modifier for increasing the selectivity, suppressing the undesirable oxidation of olefin or olefin oxide to carbon dioxide and water, relative to the desired formation of olefin oxide. Organic halides are in particular organic bromides, and more in particular organic chlorides. Preferred organic halides are chlorohydrocarbons or bromohydrocarbons. More preferably they are selected from the group of methyl chloride, ethyl chloride, ethylene dichloride, ethylene dibromide, vinyl chloride or a mixture thereof. Most preferred are ethyl chloride and ethylene dichloride.

The organic halides are generally effective as reaction modifier when used in low concentration in the feed, for example up to 0.01 mole-%, relative to the total feed. In particular when the olefin is ethylene, it is preferred that the organic halide is present in the feed at a concentration of at most 50×10^{-4} mole-%, in particular at most 20×10^{-4} mole-%, more in particular at most 15×10^{-4} mole-%, relative to the total feed, and preferably at least 0.2×10^{-4} mole-%, in particular at least 0.5×10^{-4} mole-%, more in particular at least 1×10^{-4} mole-%, relative to the total feed.

In addition to the olefin, oxygen and the organic halide, the feed may contain one or more optional components, for example carbon dioxide, inert gases and saturated hydrocarbons. Carbon dioxide is a by-product in the epoxidation process. However, carbon dioxide generally has

an adverse effect on the catalyst activity. Typically, a concentration of carbon dioxide in the feed in excess of 25 mole-%, preferably in excess of 10 mole-%, relative to the total feed, is avoided. A concentration of carbon dioxide as low as 1 mole-% or lower, for example 0.5 mole-%, relative to the total feed, may be employed. Inert gases, for example nitrogen or argon, may be present in the feed in a concentration of from 30 to 90 mole-%, typically from 40 to 80 mole-%. Suitable saturated hydrocarbons are methane and ethane. If saturated hydrocarbons are present, they may be present in a quantity of up to 80 mole-%, relative to the total feed, in particular up to 75 mole-%. Frequently they are present in a quantity of at least 30 mole-%, more frequently at least 40 mole-%. Saturated hydrocarbons may be added to the feed in order to increase the oxygen flammability limit.

The epoxidation process may be carried out using reaction temperatures selected from a wide range. Preferably the reaction temperature is in the range of from 150 to 340 °C, more preferably in the range of from 180 to 325 °C.

In order to reduce the effects of deactivation of the catalyst, the reaction temperature may be increased gradually or in a plurality of steps, for example in steps of from 0.1 to 20 °C, in particular 0.2 to 10 °C, more in particular 0.5 to 5 °C. The total increase in the reaction temperature may be in the range of from 10 to 140 °C, more typically from 20 to 100 °C. The reaction temperature may be increased typically from a level in the range of from 150 to 300 °C, more typically from 200 to 280 °C, when a fresh catalyst is used, to a level in the range of from 230 to 340°C, more typically from 240 to 325°C, when the catalyst has decreased in activity due to aging.

The epoxidation process is preferably carried out at a reactor inlet pressure in the range of from 1000 to 3500 kPa. "GHSV" or Gas Hourly Space Velocity is the unit volume of gas at normal temperature and pressure (0 °C, 1 atm, i.e.

5 101.3 kPa) passing over one unit volume of packed catalyst per hour. Preferably, when the epoxidation process is as a gas phase process involving a packed catalyst bed, the GHSV is in the range of from 1500 to 100 00 Nl/(l.h). Preferably, the process is carried out at a work rate in the range of
10 from 0.5 to 10 kmole olefin oxide produced per m³ of catalyst per hour, in particular 0.7 to 8 kmole olefin oxide produced per m³ of catalyst per hour, for example 5 kmole olefin oxide produced per m³ of catalyst per hour.

The olefin oxide produced may be recovered from the
15 reaction mixture by using methods known in the art, for example by absorbing the olefin oxide from a reactor outlet stream in water and optionally recovering the olefin oxide from the aqueous solution by distillation. At least a portion of the aqueous solution containing the olefin oxide
20 may be applied in a subsequent process for converting the olefin oxide into a 1,2-diol, a 1,2-diol ether or an alkanolamine.

The olefin oxide produced in the epoxidation process may be converted into a 1,2-diol, into a 1,2-diol ether or into
25 an alkanolamine.

The conversion into the 1,2-diol or the 1,2-diol ether may comprise, for example, reacting the olefin oxide with water, suitably using an acidic or a basic catalyst. For example, for making predominantly the 1,2-diol and less 1,2-
30 diol ether, the olefin oxide may be reacted with a ten fold molar excess of water, in a liquid phase reaction in presence of an acid catalyst, e.g. 0.5-1.0 %w sulfuric acid, based on the total reaction mixture, at 50-70 °C at 100 kPa absolute,

or in a gas phase reaction at 130-240 °C and 2000-4000 kPa absolute, preferably in the absence of a catalyst. If the proportion of water is lowered the proportion of 1,2-diol ethers in the reaction mixture is increased. The 1,2-diol ethers thus produced may be a di-ether, tri-ether, tetra-ether or a subsequent ether. Alternative 1,2-diol ethers may be prepared by converting the olefin oxide with an alcohol, in particular a primary alcohol, such as methanol or ethanol, by replacing at least a portion of the water by the alcohol.

The conversion into the alkanolamine may comprise reacting the olefin oxide with an amine, such as ammonia, an alkyl amine or a dialkylamine. Anhydrous or aqueous ammonia may be used. Anhydrous ammonia is typically used to favour the production of monoalkanolamine. For methods applicable in the conversion of the olefin oxide into the alkanolamine, reference may be made to, for example US-A-4845296, which is incorporated herein by reference.

The 1,2-diol and the 1,2-diol ether may be used in a large variety of industrial applications, for example in the fields of food, beverages, tobacco, cosmetics, thermoplastic polymers, curable resin systems, detergents, heat transfer systems, etc. The alkanolamine may be used, for example, in the treating ("sweetening") of natural gas.

Unless specified otherwise, the organic compounds mentioned herein, for example the olefins, 1,2-diols, 1,2-diol ethers, alkanolamines and organic halides, have typically at most 40 carbon atoms, more typically at most 20 carbon atoms, in particular at most 10 carbon atoms, more in particular at most 6 carbon atoms. As defined herein, ranges for numbers of carbon atoms (i.e. carbon number) include the numbers specified for the limits of the ranges.

Having generally described the invention, a further understanding may be obtained by reference to the following

examples, which are provided for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLES

5 Table I presents information concerning the properties and geometric configuration of a Support I used in the preparation of the catalysts as described in these Examples. Support II represents another suitable support for use in this invention.

10

Table I

	Support I	Support II
Properties		
Water Absorption (%)	46.5	50.4
Bulk Packing Density (kg/m ³)	843	788
ASTM Attrition Loss (%)	14.7	16.5
Average Flat Plate Crush Strength (N)	130	180
Surface Area (m ² /g)	0.77	0.78
Geometric Configuration		
Nominal Size (mm)	8	8
Average Length (mm)	7.7	7.7
Length, Range (mm)	6.6-8.6	6.6-8.6
Diameter (mm)	8.6	8.6
Bore Diameter (mm)	1.02	1.02
Ratio Length/Outside Diameter	0.90	0.90

Catalyst preparation

Catalyst A (for comparison):

- 5 Catalyst A was prepared in two impregnation steps: the first step involving impregnation with silver, without dopants, the second step involving impregnation with silver and the dopants. Approximately 120 grams of Support I was first impregnated with 204 grams of silver solution having a
- 10 specific gravity of 1.53 g/mL. No dopants were added to the silver solution. Support I was evacuated to 20 mm Hg for 1 minute and the impregnation solution was added to Support I while under vacuum, then the vacuum was released and the carrier allowed to contact the liquid for 3 minutes.
- 15 Impregnated Support I was then centrifuged at 500 rpm for 2 minutes to remove excess liquid. Subsequently, impregnated Support I was placed in a vibrating shaker and dried in

flowing air at 250°C for 7 minutes. The resulting dried Catalyst A Precursor contained approximately 17 %w silver. The dried Catalyst A Precursor was then impregnated with a second solution which was made by mixing 191.0 grams of silver stock solution of specific gravity 1.53 g/ml with a solution of 0.2915 g of NH_4ReO_4 in 2 g of 1:1 $\text{ED}\ddot{\text{A}}/\text{H}_2\text{O}$, 0.0678 g of ammonium metatungstate dissolved in 2 g of 1:1 ammonia/water and 0.3747 g LiNO_3 dissolved in water. Additional water was added to adjust the specific gravity of the solution to 1.48 g/mL. 50 grams of such doped solution was mixed with 0.1397 g of 45.4 %w CsOH solution. This final impregnation solution was used to prepare Catalyst A. A flask containing 30 grams of the Catalyst A Precursor was evacuated to 20 mm Hg for 1 minute and the final impregnation solution was added while under vacuum, then the vacuum was released and the precursor allowed to contact the liquid for 3 minutes. The impregnated precursor was then centrifuged at 500 rpm for 2 minutes to remove excess liquid. Subsequently, Catalyst A was placed in a vibrating shaker and dried in air flowing at a rate of 217 Nml/min. at 250°C for 7 minutes. The final Catalyst A composition was 27.3% Ag, 550 ppm Cs/g catalyst, 2.4 μmole Re/g catalyst, 0.60 μmole W/g catalyst, and 12 μmole Li/g catalyst.

Catalyst B (according to the invention):

Catalyst B was prepared in two impregnation steps: the first step involving impregnation with silver and a tungsten dopant, the second step involving impregnation with silver and the other dopants. Ammonium metatungstate (0.0639 g) was first dissolved in 1 gram of 33 %w ethylenediammine/water mixture. This solution was added to 200 grams of a silver solution having a specific gravity of 1.523 g/ml. Support I was impregnated with this silver solution, then centrifuged and dried according to the procedure for Catalyst A

Precursor. The resulting dried Catalyst B Precursor contained approximately 16.6 %w silver. This dried Catalyst B Precursor was then impregnated with a second solution which was made by mixing 200 grams of silver stock solution of specific gravity 1.523 g/ml with a solution of 0.2906 g of NH_4ReO_4 in 1 g of 1:1 EDA/ H_2O , and 0.3735 g LiNO_3 dissolved in 1 gram water. Additional water was added to adjust the specific gravity of the solution to 1.49 g/ml. 50 grams of such doped solution was mixed with 0.1416 g of 44.6 %w CsOH solution. This final impregnation solution was used to prepare Catalyst B. A flask containing 30 grams of the Catalyst B Precursor was evacuated to 20 mm Hg for 1 minute and the final impregnation solution was added to the Catalyst B Precursor while under vacuum, then the vacuum was released and the Precursor allowed to contact the liquid for 3 minutes. The impregnated Catalyst B Precursor was then centrifuged at 500 rpm for 2 minutes to remove excess liquid, and subsequently placed in a vibrating shaker and dried in air flowing at a rate of 21.7 NL/min at 250°C for 7 minutes. The final Catalyst B composition was 27.3% Ag, 560 ppm Cs/g catalyst, 2.4 $\mu\text{mole Re/g catalyst}$, 0.60 $\mu\text{mole W/g catalyst}$, and 12 $\mu\text{mole Li/g catalyst}$.

Catalyst testing

Catalysts A and B were tested for their ability to produce ethylene oxide from a feed containing ethylene and oxygen. To do this, samples of the crushed catalysts, containing 5.29 g silver, were each loaded into a 6.4 mm (1/4 inch) stainless steel U-shaped tube reactor tube. The tube was immersed in a molten metal bath (heat medium) and the ends were connected to a gas flow system. The weight of catalyst used and the inlet gas flow rate were adjusted to give a gas hourly space velocity of 3300 NL/(1.h) , as calculated for uncrushed catalyst. The inlet gas pressure

was 1550 kPa. The catalysts were treated with nitrogen at 225°C for 2 hours prior to testing. The testing gas mixture passed through the catalyst bed, in a "once-through" operation, consisted of 30 %v ethylene, 8 %v oxygen, 5 %v carbon dioxide, 57 %v nitrogen and 1.5 to 6.0 parts by million by volume (ppmv) ethyl chloride. Ethyl chloride concentration was adjusted to obtain maximum selectivity. The temperature was adjusted to achieve a concentration of ethylene oxide of 3.1 %v in the reactor outlet.

The initial performance, selectivity in %-mole and activity in °C, of the catalysts is reported in Table II. The activity is the temperature at which the concentration of ethylene oxide in the reactor outlet is 3.1 %v; a lower temperature indicates a higher activity. The initial performance reflects the performance level of the catalyst as it lined out during the initial two-weeks of testing.

The activity and selectivity were also measured upon continued operation. The results obtained after a cumulative production of ethylene oxide of 0.6 kton/m³ and 1.4 kton/m³ of catalyst are also reported in Table II.

Table II

	Selectivity, %-mole	Activity, °C
Catalyst A *)		
Initial performance	89.0	246
Performance at 0.6 kton/m ³	88.0	264
Performance at 1.4 kton/m ³	81.0	278
Catalyst B **)		
Initial performance	87.5	248
Performance at 0.6 kton/m ³	87.0	254
Performance at 1.4 kton/m ³	79.5	268
*) for comparison		
**) according to the invention		

Comparing Catalyst A with Catalyst B illustrates that the initial catalyst activity can be maintained with
 5 respectable initial selectivity when the dopant addition is sequenced between two impregnation steps.

The performance data obtained for the Catalysts A and B at a cumulative ethylene oxide production of 0.6 kton/m³ and 1.4 kton/m³ indicate that Catalyst B provides an advantage
 10 with respect to stability over Catalyst A. The improvement in activity stability is evident from the data in Table II.

While this invention has been described in terms of the presently preferred embodiment, reasonable variations and modifications are possible by those skilled in the art. Such
 15 variations and modifications are within the scope of the described invention and the appended claims.

C L A I M S

1. A process for preparing a catalyst comprising silver, a rhenium component, and a rhenium co-promoter on a support, which process comprises
 - depositing the rhenium co-promoter on the support prior to or simultaneously with depositing silver on the support, and
 - depositing the rhenium component on the support after depositing silver on the support.
2. A process as claimed in claim 1, wherein the rhenium co-promoter is selected from components comprising one or more of tungsten, chromium, molybdenum, sulfur, phosphorus, boron and mixtures thereof, in particular tungsten.
3. A process as claimed in claim 1 or 2, wherein the rhenium is deposited in a quantity in the range of from 0.01 to 50 mmole/kg, in particular 0.1 to 10 mmole/kg, calculated as the quantity of rhenium relative to the weight of the catalyst.
4. A process as claimed in any of claims 1-3, wherein the rhenium co-promoter is deposited in a total quantity in the range of from 0.01 to 50 mmole/kg, in particular 0.1 to 10 mmole/kg, calculated as the elements relative to the weight of the catalyst.
5. A process as claimed in any of claims 1-4, wherein silver is deposited in a quantity in the range of from 100 to 400 g/kg, relative to the weight of the catalyst.
6. A catalyst comprising silver, a rhenium component, and a rhenium co-promoter deposited on a support which catalyst is obtainable by the process for preparing a catalyst as claimed in any of claims 1-5.
7. A process for preparing an olefin oxide by reacting an olefin with oxygen in the presence of a catalyst which is obtainable by the process for preparing a catalyst as claimed in any of claims 1-5.

8. A method of using an olefin oxide for making a 1,2-alkanediol, a 1,2-alkanediol ether or a 1,2-alkanolamine comprising converting the olefin oxide into the 1,2-alkanediol, the 1,2-alkanediol ether, or the 1,2-alkanolamine, wherein the olefin oxide has been obtained by the process for preparing an olefin oxide as claimed in claim 7.

INTERNATIONAL SEARCH REPORT

Inter	Application No
PC 17052005/010996	

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B01J23/68 B01J37/02 C07D301/10 C07C213/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2004/101144 A (SHELL OIL COMPANY; MATUSZ, MAREK; RICHARD, MICHAEL, ALAN; LOCKEMEYER,) 25 November 2004 (2004-11-25) example E page 17, line 24 - line 26	1-8
X	US 4 766 105 A (LAURITZEN ET AL) 23 August 1988 (1988-08-23) cited in the application column 14, line 15 - line 37 claims 2,21	1-7
X	US 5 663 385 A (KEMP ET AL) 2 September 1997 (1997-09-02) column 12, line 1 - line 20 claims 1,2	1-7
	----- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents:**

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- *Z* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Intern Application No
PCT/US2005/010996

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 380 697 A (MATUSZ ET AL) 10 January 1995 (1995-01-10) cited in the application example D; table 1 -----	1-7
X	EP 0 716 884 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V; SHELL INTERNATIONALE R) 19 June 1996 (1996-06-19) examples D,F -----	1,3-7
X	US 4 845 296 A (AHMED ET AL) 4 July 1989 (1989-07-04) cited in the application the whole document -----	8

INTERNATIONAL SEARCH REPORT

Intern Application No
PCT/US2005/010996

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004101144 A	25-11-2004	US 2004224841 A1 US 2004260103 A1 WO 2004101144 A1	11-11-2004 23-12-2004 25-11-2004
US 4766105 A	23-08-1988	AT 69977 T AU 592478 B2 AU 8053987 A BG 60854 B1 BR 8705810 A CA 1304346 C CN 87107194 A ,B CS 8806977 A2 CS 8707729 A2 DE 3774999 D1 DK 560087 A EG 18719 A EP 0266015 A1 ES 2028860 T3 FI 874786 A ,B, GR 3003662 T3 HU 47046 A2 IE 60557 B1 IL 84232 A IN 169589 A1 JP 2619660 B2 JP 63126552 A KR 9611047 B1 MA 21096 A1 MX 170627 B NO 874528 A ,B, NZ 222342 A PH 25304 A PL 268522 A1 PT 86038 A ,B RO 100109 A2 SG 126392 G SU 1831369 A3 TR 26675 A US 4820675 A US 4808738 A YU 180088 A1 YU 197887 A1 ZA 8708013 A	15-12-1991 11-01-1990 05-05-1988 31-05-1996 31-05-1988 30-06-1992 27-07-1988 12-09-1990 13-06-1990 16-01-1992 01-05-1988 30-12-1993 04-05-1988 16-07-1992 01-05-1988 16-03-1993 30-01-1989 27-07-1994 21-06-1992 16-11-1991 11-06-1997 30-05-1988 16-08-1996 01-07-1988 31-08-1993 02-05-1988 27-09-1989 30-04-1991 08-12-1988 01-11-1987 02-12-1991 19-02-1993 30-07-1993 05-07-1994 11-04-1989 28-02-1989 28-02-1990 31-12-1988 29-06-1988
US 5663385 A	02-09-1997	US 5545603 A DE 69521329 D1 DE 69521329 T2 WO 9613329 A1 EP 0789622 A1 ES 2158133 T3 JP 10507964 T	13-08-1996 19-07-2001 08-11-2001 09-05-1996 20-08-1997 01-09-2001 04-08-1998
US 5380697 A	10-01-1995	AT 164784 T AU 680299 B2 AU 7695194 A BR 9407417 A CA 2171213 A1 CN 1133571 A ,C	15-04-1998 24-07-1997 27-03-1995 12-11-1996 16-03-1995 16-10-1996

INTERNATIONAL SEARCH REPORT

Interna Application No
PCT/US2005/010996

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5380697	A	CZ 9600729 A3	11-09-1996
		DE 69409536 D1	14-05-1998
		DE 69409536 T2	30-07-1998
		DK 717659 T3	21-12-1998
		WO 9507139 A1	16-03-1995
		EP 0717659 A1	26-06-1996
		ES 2114225 T3	16-05-1998
		FI 961030 A	06-03-1996
		JP 9502129 T	04-03-1997
		NO 960915 A	06-05-1996
		NZ 273597 A	28-10-1996
		PH 30949 A	23-12-1997
		PL 313355 A1	24-06-1996
		RU 2126296 C1	20-02-1999
		SG 81876 A1	24-07-2001
		SK 30496 A3	01-10-1996
		TR 28524 A	30-09-1996
		ZA 9406841 A	24-04-1995
EP 0716884	A	19-06-1996	DE 69520409 D1
			DE 69520409 T2
			EP 0716884 A2
			ES 2155111 T3
			JP 8224477 A
US 4845296	A	04-07-1989	NONE